

JAPANESE

[JP,08-085174,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE

[Translation done.]

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**DETAILED DESCRIPTION**

[Detailed Description of the Invention]

[0001]

[Industrial Application]In detail this invention about a multilayer blow molding object Automotive fuel (gasoline). It is related with the multilayer blow molding object of a light-gage light weight which is excellent in reuse (reclaimed rubber) nature, such as a barricade generated in the case of the barrier (prevention from penetration) performance and the resisting pressure characteristic to the gasoline (gasohol) containing the mixture of hydrocarbon and an oxygen content organic compound, for example, alcohol, or its manufacture.

[0002]

[Description of the Prior Art]The trial of plastic-izing by a blow molding method has been performed from before from the purpose that the fuel tank of a car raises the flexibility of the improvement in safety at the time of a shock, or shape conventionally etc. Excelling in mechanical strengths as the permeation preventing performance (gas barrier property) to fuel and a tank, such as shock resistance, as the characteristic required of a resin made fuel tank is mentioned. On the other hand, polyolefine is comparatively cheap, since it excels in shock resistance or a mechanical strength, it is suitable as a plastic-ized material, but there is a problem of being inferior to gas barrier property, and various improvement is proposed.

[0003]For example, the method of carrying out the chemical treatment of the inner surface of the tank made from polyolefine by fluorine gas (F<sub>2</sub>) or sulfone gas (SO<sub>3</sub>),

In the denaturation polyamide which compounded the polyolefine which carried out alkyl carboxylation to the polyamide which is comparatively excellent in barrier nature, the lamina method of making these forming in layers into the continuation matrix phase of polyolefine etc. are mentioned. However, by these methods, this use is not yet enough as barrier nature, The correspondence to the laws and regulations to be further tightened for the purpose of environmental protection from now on is difficult, the stratified gestalt of the denaturation polyamide formed further is not

easily stabilized due to a process condition, there is also a problem on which shock resistance is reduced, and a perfect method cannot be said.

[0004]On the other hand, by a chemical treatment method, there are the endurance of processing and an environmental problem at the time of processing. As indicated, for example to JP,1-14049,B, Material excellent in the gas barrier property of polyamide system resin, an ethylene-vinyl acetate copolymer saponification thing or thermoplastic polyester, etc., etc. is made into a barrier layer, and the multilayering method which laminates this and the polyolefine which is main strata via the glue line which consists of denaturation polyolefine is proposed. The gas barrier property of the Plastic solid acquired becomes the dramatically outstanding thing, and utilization is following this multilayering method as most effective method in the plastic-ized method of the fuel tank of a car. However, this method needs to be a specific ratio, without reducing mechanical strengths, such as shock resistance, and to return stably recycled materials, such as a multilayer barricade generated at the time of shaping, to a raw material from an economic viewpoint, for example at about 50% of the weight of a rate. In respect of the manufacturing cost, it has left the technical problem, and it is necessary to make it low cost further, and it is possible to carry out the weight saving of the tank itself more, maintaining reclaimed rubber nature, such as a barricade generated at the time of the performance needed for the resin made fuel tank for cars for the purpose, or manufacture. However, development of a material excellent in rigidity is needed as a measure against the fall of the pressure resistance nature of the tank accompanying thinning itself, or shape retentivity, and there is nothing that was completed as a tank still satisfied under the present circumstances.

[0005]  
[Means for Solving the Problem]This invention persons are excellent in mechanical strengths, such as gas barrier property and pressure resistance nature which are the conditions required of an automotive fuel tank etc., and shock resistance, in view of this actual condition, and reclaimed rubbers, such as a barricade, are possible for them, And as a result of inquiring wholeheartedly for the purpose of providing a multilayer hollow body in which the light-gage weight saving was carried out by high rigidity, by using a specific polyethylene composition composite-ized by an inorganic filler as a polyethylene layer used as a main stratum, it finds out that this purpose is attained and came to complete this invention.

[0006]Namely, a polyethylene layer and a barrier layer constituted with one sort or two sorts or more of mixtures of polyamide system resin, an ethylene-vinyl acetate copolymer saponification thing, and thermoplastic polyester, In a multilayer blow molding object fabricated from a charge of a multilayer laminated material which it comes to laminate via a glue line constituted by modified-polyolefin-resin layer, Or all are constituted by polyethylene composition containing 60 to polyethylene 95 weight section and five to inorganic filler 40 weight section which denaturalized with unsaturated carboxylic acid or its anhydride. [ this polyethylene layer ]

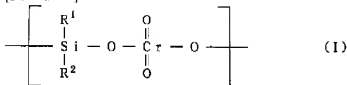
[0007]  
[Detailed Description of the Invention]  
(1) As a polyethylene component of the polyethylene composition which constitutes the polyethylene layer of the multilayer blow molding object in polyethylene layer  
\*\* polyethylene this invention, a highroad melt flow rate (190 \*\*, 21.6 kg loads) -- 1-10g/-- it is 3-8g/10 minutes preferably, and the thing of 940 - 970 kg/m<sup>3</sup> has [ more than 935 kg/m<sup>3</sup> ] preferably desirable density for 10 minutes. In 1g/less than 10 minutes, it becomes difficult to uniform knead the highroad melt flow rate of polyethylene with an inorganic filler, the extrusion nature and the moldability at the time of blow molding worsen, and if it exceeds 10g/10 minutes, the moldability at the time of blow molding (drawdown nature) will worsen too. When high rigidity-

ization of a multilayer blow molding object becomes it difficult that the density of polyethylene is less than 935 kg/m<sup>3</sup> and 970 kg/m<sup>3</sup> is exceeded, it is in the tendency for shock resistance to fall.

[0008] Various kinds of polyethylene which can use various polyethylene, for example, is manufactured with a Ziegler type catalyst as polyethylene which has the above-mentioned physical properties, the polyethylene manufactured with a high voltage radical method, the polyethylene manufactured by a chromium catalyst, etc. can be mentioned. Also in these, the polyethylene manufactured by a chromium catalyst is preferred.

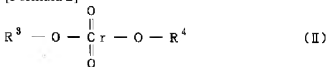
[0009] Following formula: CrO<sub>3</sub> which is indicated as a chromium catalyst in the Phillips catalyst expressed with CrO<sub>3</sub>, for example and the catalyst for which it makes it come to return a chromium catalyst with a reducing agent, for example, JP, 44-2996, B, 44-3827, a 47-1766 gazette, etc., [0010]

[Formula 1]



[0011] (as for R<sup>1</sup> and R<sup>2</sup>, a carbon number shows the hydrocarbon group of 1-14 among) a formula -- or [0012]

[Formula 2]

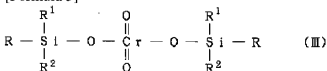


[0013] A thing using a chromium catalyst and a reducing agent which are expressed with (a carbon number shows a steric exclusion multi-alicyclic hydrocarbon group of 7-20 among a formula, as for R<sup>3</sup> and R<sup>4</sup>) is preferred.

[0014] as an especially desirable chromium compound -- following formula: CrO<sub>3</sub> --

or [0015]

[Formula 3]

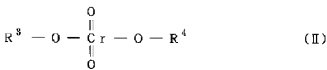


[0016] the inside of a formula, R and R<sup>1</sup>, and R<sup>2</sup> -- a carbon number -- the hydrocarbon group of 1-14. the hydrocarbon group which contains 3-10 carbon atoms preferably -- being shown -- it being BISUTORI hydrocarbonyl silyl chromate expressed, and, Screw triphenylsilyl chromate, BISUTORIMECHIRU naphthyl silyl chromate, BISUTORIECHIRU phenylsilyl chromate, screw trinaphthyl silyl chromate, screw trixyl silyl chromate, screw tritolyl silyl chromate, etc. are mentioned as an example. Screw triphenylsilyl chromate is mentioned as most desirable thing also in these.

[0017] Other desirable examples of a chromium compound are dialkyl chromate expressed with following formula (II). For example, JIADA man chill chromate (following formula (IV)), di-2-alkyl bornyl chromate (following formula (V)), di-2-alkyl fenchyl chromate (following formula (VI)), etc. are mentioned. The most desirable thing also in these is JIADA man chill chromate.

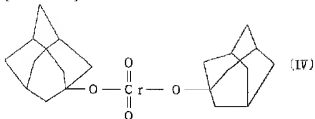
[0018]

[Formula 4]



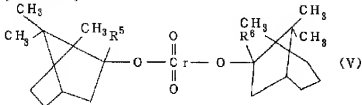
[0019]

[Formula 5]



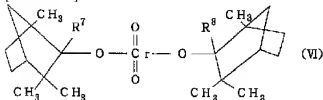
[0020]

[Formula 6]



[0021]

[Formula 7]



[0022](Among the above-mentioned formula, a carbon number shows the steric exclusion multi-alcyclic hydrocarbon group of 7-20, and, as for R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, and R<sup>8</sup>, R<sup>3</sup> and R<sup>4</sup> show a hydrocarbon group)

[0023]Generally, these chromium catalysts make porosity inorganic oxides, such as silica, support the above-mentioned chromium compound, and are used for them. What is produced by returning with a reducing agent is preferred, and this chromium catalyst is general formula: R'<sup>x</sup>Al(OR'')<sup>y</sup> (for the integer of 1 or 2, x and y are 3 and the sum total) as a reducing agent in that case. R' and R'' show the hydrocarbon group containing 1-14 carbon atoms. The alkylaluminum alkoxide expressed is preferred. As a kind of hydrocarbon group, an alkyl group, an aralkyl group, an aryl group, the Al Caleel group, alicyclic, a bicyclic type, a similar hydrocarbon group, etc. can be mentioned. These reducing agents can also be used as two or more sorts of mixtures, even if independent. About a catalyst presentation, the mole fraction (it is written as an aluminum/Cr ratio below) of the aluminium atoms in a reducing agent and the chromium atom in a silyl chromate compound is 100-0.5, and it is 15:0.5 preferably, and is 5.0-1.0 especially preferably.

[0024]As a polymerization method of ethylene using these catalysts, Techniques, such as the method of polymerizing in publicly known suspension polymerization and solution polymerization, for example, the gaseous phase as shown in JP,60-1882, B, can be applied, and copolymerization with one sort or two sorts or more of alpha olefins is possible in addition to ethylene homopolymerization. As alpha olefin, a carbon number is 3-10 pieces, and, for example Propylene, They are butene-1, the pentene- 1, the 3-methylbutene 1, the hexene- 1, 4-methylpentene- 1, the 4-

methylhexane 1, the 4,4-dimethylpentene- 1, the heptene- 1, the octene- 1, the nonene- 1, and decene 1 grade, Propylene, butene-1, the hexene- 1, 4-methylpentene- 1, and the octene- 1 are mentioned preferably.

[0025]As described above, use of polyethylene manufactured by a chromium catalyst is preferred, but it is also possible to use together polyethylene manufactured by other polyethylene, for example, a Ziegler catalyst, a radical catalyst, etc. if needed.

[0026]\*\* Modified polyethylene is prepared by denaturalizing polyethylene which carried out the modified polyethylene above with unsaturated carboxylic acid or its anhydride. As unsaturated carboxylic acid used for denaturation, or its anhydride, Dicarboxylic anhydrides, such as dicarboxylic acid, such as monocarboxylic acid, such as acrylic acid and methacrylic acid, maleic acid, boletic acid, and itaconic acid, a maleic anhydride, and itaconic acid anhydride, are mentioned, and acrylic acid or a maleic anhydride is especially preferred. In order to improve the compatibility of denatured polyethylene and the after-mentioned inorganic filler blended with it, it is desirable for polyethylene to denaturalize so that unsaturated carboxylic acid or its anhydride may contain 0.01 to 2% of the weight preferably 0.005 to 5% of the weight. Since an effect of compatibility improvement of unsaturated carboxylic acid in polyethylene or content of the anhydride in less than 0.005 % of the weight is not demonstrated, it is not desirable, and if it exceeds 5 % of the weight, cost of the compatibility improvement effect formal meeting for engagement becomes high, and is not preferred from a viewpoint of economical efficiency.

[0027]Methods of denaturation include a method of carrying out melt kneading of polyethylene, unsaturated carboxylic acid, or its anhydride in an extrusion machine, a method of adding unsaturated carboxylic acid or its anhydride in polyethylene currently suspended in suitable carrier fluid, and carrying out heating churning, etc. What denaturalized directly the whole polyethylene which uses modified polyethylene for formation of a polyethylene layer, What manufactured beforehand unsaturated carboxylic acid or high modified polyethylene (henceforth high concentration modified polyethylene) of content of the anhydride, mixed this with native polyethylene, and adjusted arbitrarily a denaturation degree (content of unsaturated carboxylic acid or its anhydride) may be used.

[0028]\*\* As an inorganic filler ingredient blended with the inorganic filler above-mentioned modified polyethylene, Mica, a fibrous filler, talc, a calcium silicate (wollastonite), calcium carbonate, barium sulfate, alumina, magnesium carbonate, titanium oxide, silica, kaolin, carbon black, etc. are mentioned. There are kinds, such as white mica, golden mica, and black mica, and a thing from which a process differs in mica, and although it is usable in all, white mica and golden mica of wet milling or wet classification are mentioned as a desirable thing from a point of the rigid improvement effect of a cost formal meeting for engagement. Glass fiber, carbon fiber, an aramid fiber, a potassium titanate fiber, basic magnesium sulfate fibers, calcium carbonate textiles, calcium silicate fibers, etc. are mentioned to a fibrous filler as a desirable thing. These inorganic fillers can be used combining one sort or two sorts or more.

[0029]0.1-1500 micrometers of mean particle diameter of these inorganic fillers are 0.1-500 micrometers preferably -- and an average aspect ratio -- 1-300 -- a thing of 5-200 is preferably suitable. Especially, as a desirable example, mean particle diameter is 8-100 micrometers, and an average aspect ratio is the mica of 10-100, and mean particle diameter is 8-13 micrometers, and glass fiber of 5-100 is mentioned for an average aspect ratio.

[0030]A thing of less than a mentioned range has mean particle diameter and an average aspect ratio in a tendency which becomes insufficient | the rigidity

improvement effect of a multilayer blow molding object ], and on the other hand, when a mentioned range is exceeded, it is in a tendency which becomes easy to spoil a fall and reclaimed rubber nature of mechanical strengths, such as impact strength. A surface-active agent of various kinds [ purpose / of improvement in compatibility with polyethylene ]; Epoxysilane, such as gamma-glycidoxypolytrimetoxysilane. The Silang system coupling agents, such as aminosilanes, such as vinylsilane, such as vinyl trichlorosilane, and gamma-aminopropyl triethoxysilane; an inorganic filler by which the surface treatment was carried out with metallic soap etc. can be especially used as a suitable thing.

[0031]\*\* A polyethylene composition used by polyethylene composition this invention is obtained by mixing the above-mentioned inorganic filler with the above-mentioned modified polyethylene. Preparation of a polyethylene composition modified polyethylene (a mixture of high concentration modified polyethylene and native polyethylene is included), and an inorganic filler, For example, after mixing by Henschel type mixer, a ribbon blender, etc. beforehand, it can carry out by extruding out melt kneading using the usual kneading machines, such as a 1 axis extrusion machine, a twin screw extruder, a Banbury mixer, a roll mixer, and a kneader. In this case, it is preferred to perform high kneading comparatively and kneading and a granulation using a twin screw extruder are usually performed so that distribution of each ingredient may be performed good. Although the kneading can supply modified polyethylene and an inorganic filler to a mixer simultaneously and can perform them, For example, when using mica and glass fiber, in order to avoid breakage by the kneading, it is preferred to supply and knead an inorganic filler from a feeding mouth which carried out the provisioning process of the modified polyethylene to the first portion of a twin screw extruder, and was provided subsequently to a latter half part of this extrusion machine. With such a technique, the rigidity of a blow molding object and shock-proof improvement can be aimed at.

[0032]Modified polyethylene is 70 to 95 % of the weight preferably 60 to 95% of the weight, and an inorganic filler of modified polyethylene in a polyethylene composition and a rate of an inorganic filler is 5 to 30 % of the weight preferably five to 40% of the weight. At less than 5 % of the weight, an effect of rigidity improvement of a multilayer blow molding object is deficient in a rate of an inorganic filler. In an excess of 40 % of the weight, it falls remarkably, and in blow molding, parison is further torn at the time of a blow up, or it becomes insufficient weld in a pinch off part and welding mechanical properties and reclaimed rubber nature, such as shock resistance, of fabricating parts.

[0033](2) As resin which constitutes a barrier layer of a multilayer blow molding object of barrier layer this invention, it is chosen out of polyamide system resin, an ethylene-vinyl acetate copolymer saponification thing, or thermoplastic polyester as one sort or two sorts or more of mixtures. As polyamide, hexamethylenediamine, decamethylenediamine, Dodecamethylenediamine, 2,2,4-, or 2,4,4-trimethyl hexamethylenediamine, 1,3- or 1,4-bis(aminomethyl)cyclohexane, a screw (p-aminocyclohexyl methane), m- or aliphatic series like p-xylylene diamine, alicycle fellows, or aromatic diamine and adipic acid, Suberic acid, sebacic acid, cyclohexanedicarboxylic acid, terephthalic acid, Polyamide resin; 6-aminocaproic acid manufactured from aliphatic series like isophthalic acid, alicycle fellows, or aromatic dicarboxylic acid, Polyamide resin manufactured from 11-aminoundecanoic acid and aminocarboxylic acid like 12-amino dodecanoic acid; Epsilon caprolactam, A mixture of copolymerization polyamide resin; which consists of polyamide resin; manufactured from omega-dodecalactam and omega-RAURO lactam and these ingredients, or these polyamide resin is mentioned.

[0034]Specifically, a copolymer of nylon 6, Nylon 66, Nylon 610, Nylon 11, Nylon

12, Nylon 612, Nylon 46, Nylon MXD 6, and nylon 6 / 66 grades is mentioned. Furthermore, from the purpose of superiors for adhesive properties, to such polyamide Ethylene, propylene, Olefin system elastomers (for example, an ethylene propylene copolymer, an ethylene butene copolymer, etc.) which are two sorts or three sorts or more of copolymer rubbers of alpha olefins, such as butene-1, the hexene- 1, and 4-methyl-pentene, with unsaturated carboxylic acid or its anhydride. It is possible to blend what denaturalized and this is that [ one ] of a suitable mode in this invention.

[0035]As an ethylene-vinyl acetate copolymer saponification thing (saponification EVA), Although the chemical composition is not limited, what is obtained when it thinks from fuel barrier nature, and in the degree of saponification an ethylene content saponifies 25-50-mol% of an ethylene-vinylacetate copolymer not less than 93% so that it may become not less than 96% preferably is preferred.

[0036]As thermoplastic polyester, it is what is obtained by condensation of saturation dibasic acid and glycols, For example, ethylene glycol and polyethylene terephthalate obtained from terephthalic acid; Phthalic acid, Isophthalic acid, sebacic acid, adipic acid, azelaic acid, glutaric acid, Saturation dibasic acid, such as succinic acid and oxalic acid, as polyethylene terephthalate copolymer; used as a copolymer component, and a diol component 1, 4-cyclohexane dimethanol, Polyethylene terephthalate copolymer; which used a diethylene glycol, propylene glycol, etc. as a copolymer component, or poly tetramethyl terephthalate which used 1,4-butanediol as a copolymer component is mentioned.

[0037](3) Polyolefine which denaturalized with the above-mentioned unsaturated carboxylic acid or its anhydride like modified polyethylene used for the above-mentioned polyethylene composition as denaturation polyolefine which constitutes a glue line of a multilayer blow molding object of glue line this invention is used. As polyolefine which denaturalizes with unsaturated carboxylic acid or its anhydride, although polyolefines, such as an ethylene homopolymer, an ethylene-alpha olefin copolymer, and polypropylene, are mentioned, It is preferred to use a polyethylene layer which constitutes a main stratum, and a thing of the same kind from a viewpoint of improving an adhesive property. As for unsaturated carboxylic acid in denaturation polyolefine, or content of the anhydride, it is preferred that unsaturated carboxylic acid adds by 0.005 to 10% of the weight of within the limits. It can carry out like a method of the denaturation of the above-mentioned polyethylene as the method of denaturation. What manufactured beforehand unsaturated carboxylic acid or high denaturation polyolefine of content of the anhydride, mixed this with native polyolefine, and prepared a denaturation degree arbitrarily in addition to a method of denaturalizing directly the whole polyolefine used for formation of a glue line may be used.

[0038](4) To resin of above-mentioned each class in additional ingredient this invention, an effect of this invention in the range which is not spoiled remarkably. An olefin system polymer, for example, polypropylene, besides various kinds of additive agent, such as an antioxidant, an ultraviolet ray absorbent, thermoforming stabilizer, colorant, lubricant, fire retardant, a spray for preventing static electricity, and a nucleating additive, ethylene-propylene rubber, etc. can be blended if needed.

[0039](5) A multilayer blow molding object of multilayer blow molding object this invention, Using the above-mentioned class resin, a polyethylene composition layer and polyamide system resin, A layer chosen from an ethylene-vinyl acetate copolymer saponification thing or thermoplastic polyester is what has a multilayer lamination form included as lamination with a fundamental three-layer gestalt pasted up via a modified-polyolefin-resin layer, As a multilayer layered product including such a three-layer gestalt, three-sort five layers constituted in order of a polyethylene composition layer / glue line / barrier layer / glue line / polyethylene composition

layer are mentioned as a desirable thing. Thickness of each class is suitably set up by the purpose of use according to gas barrier property, a mechanical strength, and other military requirements. For example, as for a barrier layer and a glue line, speaking of a fuel tank of a car, it is common respectively to be set as a lamination rate of about 2 to 4% of the whole layered product thickness. It is in a tendency which will become insufficient [ gas barrier property ] if a lamination rate will be less than 2%, and becomes difficult [ a fabricating operation ]. Since cannot expect an effect that gas barrier property is improved further, but a fall of a mechanical strength is brought about on the contrary, and it becomes a cost hike of material further and a rate of a barrier material in the case of reclaimed rubber increases even if it exceeds 4%, it is not desirable.

[0040]Manufacture of a multilayer blow molding object of this invention is supplied to each extrusion machine which connects to a blow molding machine resin which constitutes above-mentioned each class, Multilayer melting parison of uniform lamination which does not have disorder between each class through a multilayer extrusion die is extruded after melting plasticization, and it is obtained by carrying out blow molding within a metallic mold which has desired shape. About a barricade generated at the time of shaping, a layer of only one layer of the multilayer molding materials or a barricade can be added, and reclaimed rubber of the barricade can be carried out. Usually, after machinery grinding is carried out, a generated barricade carries out melt kneading with a 2 axis kneading machine etc., and reproduced-pellets. Virgin pellets of polyethylene are mixed in 10 to 50% of the weight of the range, and reclaimed rubber of this reproduced pellet is carried out to a raw material which constitutes a polyethylene layer.

[0041]Since a barricade generated at the time of manufacture of a multilayer blow molding object is a multilayer gestalt which usually contains barrier resin, When it fuses after grinding this for reclaimed rubber, a multilayer blow molding object from a resin material which barrier resin was not finely distributed in melt, therefore reused a barricade has the problem that a mechanical strength falls. If high shear is applied at the time of melt kneading of a barricade in order to carry out fine dispersion of the barrier resin, Heat deterioration of barrier resin itself [ the amount polyethylene of polymers or ] was produced, a physical-properties fall was caused, and by low shear, barrier resin was not finely distributed by distributed particle diameter of 100 micrometers or less at least as melt kneading is insufficient, but similarly a physical-properties fall was caused, and perfect reclaimed rubber was not finished conventionally. However, a barricade generated at the time of multilayer hollow body manufacture of this invention, After grinding this, carrying out melt kneading of the barrier resin that it should distribute finely and considering it as a reproduced pellet, even if it usually carries out reclaimed rubber continuously at less than 50% of the weight of a rate to a polyethylene layer raw material, there are very few physical-properties falls of a mechanical strength of a Plastic solid acquired, etc.

[0042]

[Example]Hereafter, an example explains this invention concretely.

The polyethylene manufactured by the following methods was used as Example 1 - 16(1) polyethylene-layer \*\* polyethylene polyethylene.

(i)PE-referring to the example of manufacture JP,47-1766,B of 1, and, It is 785 g of silica (made in Devi Son "952" in mean particle diameter of 50 micrometers) to 4 l. of drying hexane. [ sift out and ] The catalyst composition of the aluminum/Cr ratio 1.5 was prepared using what was calculated for 24 hours, 20 g of screw triphenylsilyl chromate, and 6 g of diethyl aluminium ethoxyide at 300 \*\*. Using this catalyst, by fluidized bed gas phase polymerization process publicly known at JP,60-1882,B. The polymerization temperature of 99 \*\*, ethylene partial pressure 1.3MPa, and hydrogen by the division ratio 0.02 with ethylene. As comonomer,



copolymerization was performed, butene-1 was comonomer by the division ratio 0.006 with ethylene, and polyethylene (it is written as PE-1 below) which is an ethylene butene-1 copolymer of density  $948 \text{ g/m}^3$  was obtained for the highroad melt flow rate 5g/10 minutes.

[0043](ii)PE-the example <manufacture of a catalyst> of 2 JP,51-112891,A was referred to, and the chromium oxide catalyst of 0.5 % of the weight of chromium support rates and 3.5 % of the weight of titanium support rates was prepared. Using this catalyst, by publicly known fluidized bed gas phase polymerization process in this gazette The polymerization temperature of  $109^\circ\text{C}$ , Ethylene partial pressure 1.5MPa and hydrogen with the division ratio 0.02 with ethylene, and 0.14 ppm of oxygen. As comonomer, copolymerization was performed, butene-1 was comonomer by the division ratio 0.002 with ethylene, and polyethylene (it is written as PE-2 below) which is an ethylene butene-1 copolymer of density  $957 \text{ g/m}^3$  was obtained for the highroad melt flow rate 50g/10 minutes.

[0044](iii)PE-using the hyperactive Ziegler type catalyst which consists of a titanium catalyst ingredient supported by 3 magnesium-halide content compound and an organoaluminium compound, Multi-tub continuation slurry polymerization which used n-heptane as the solvent was performed, and polyethylene (it is called PE-3 for short below) which is an ethylene butene-1 copolymer of density  $946 \text{ kg/m}^3$  was obtained for highroad melt flow rate 4.7 / 10 minutes.

[0045]\*\* Maleic anhydride denaturation processing was performed to manufacture above-mentioned PE-2 of high concentration modified polyethylene, and high concentration modified polyethylene (it is written as MPE-1) of 1.0 % of the weight of anhydrous malein contents was obtained.

[0046]\*\* The following thing was used as an inorganic filler inorganic filler. Mica: Glass fiber by which the surface treatment was carried out by the with a [ the golden mica glass fiber:mean fiber diameter of 9 micrometers and 6 mm in length ] by which the surface treatment was carried out by the aminosilane of the mean particle diameter of 90 micrometers, and the aspect ratio 50 aminosilane [0047]\*\* It kneaded so that it might become a blending ratio which shows polyethylene of the preparation above of a polyethylene composition, high concentration modified polyethylene, and an inorganic filler in Table 1, respectively, and it comonomer, and the polyethylene composition was obtained. After kneading and a granulation mixed polyethylene and high concentration modified polyethylene homogeneously beforehand, using the 2 axis kneading machine (PCM type by Ikegai Corp.), it performed melt kneading by the first portion by  $230^\circ\text{C}$  temperature conditions, and performed it by subsequently supplying an inorganic filler from the feeding mouth of a latter half part.

[0048](2) The following raw material was used as barrier layer barrier layer resin.

(i) nylon 6/66 copolymer (it is written as BR-2 below) which are polyamide resin relative viscosity (JIS K6810) 6.2, the nylon 6 (it is written as BR-1 below) which is the melting point (the DSC method) of  $225^\circ\text{C}$  and relative viscosity 4.3, and the melting point of  $195^\circ\text{C}$

(ii) The ethylene-vinyl acetate copolymer saponification thing melt flow rate ( $190^\circ\text{C}$ , 2.16 kg) 1.3g/10 minutes, and "Eval" (it is written as BR-3 below) By ethylene content Kuraray which is % of 32 mol

(iii) Polybutylene terephthalate which are thermoplastic polyester specific gravity 1.31 and the melting point of  $225^\circ\text{C}$  [Teijin, Ltd. make "C7000N"] (it is written as BR-4 below)

[0049](3) The following raw material was used as glue line glue line resin. Maleic anhydride modified polyethylene which is the highroad melt flow rate 10g/10 minutes, and density  $0.935 \text{ g/cm}^3$  (it is written as AD-1 below)

[0050](4) The polyethylene composition, glue line resin, and barrier layer resin of

the shaping above of a multilayer hollow body are used, Multilayer melting parison with three-sort 5 lamination of a polyethylene composition layer / glue line / barrier layer / polyethylene composition layer from the multilayer die of a multilayer blow molding machine ("NB60G" by the Japan Steel Works, Ltd.) A co-extrusion, Four kinds of multilayer blow molding objects in which the content volume of 70 l. differs from 5 kg of superintendent officers' barrier layer (thick about 120 micrometers) were acquired by closing a metallic mold and performing blow molding. The thickness of each Plastic solid was about 5-mm thickness, and the composition of each class was polyethylene layer / glue line / barrier layer =91:6:3.

[0051](5) reclaimed rubber -- the grinder (since \*\* Ironworker make, a mesh pass with a bore diameter  $\phi$  of 7 mm) ground the multilayer shaping barricade generated simultaneously next, respectively, and the grinding article with a diameter of an average crushed grain of about 2 mm was obtained. This grinding article was given with 2 axis kneading type (Japan Steel Works [ , Ltd. ], Ltd. make TEX44mmphi), melt kneading was performed on condition of the screw speed of 250 rpm, the exit resin temperature of 280 \*\*, discharge quantity 55 kg/hr, and specific energies 0.3-0.4, and the reproduced pellet was obtained. Each distributed particle diameter of barrier layer resin in these reproduced pellets was 100 micrometers or less in observation by optical microscope.

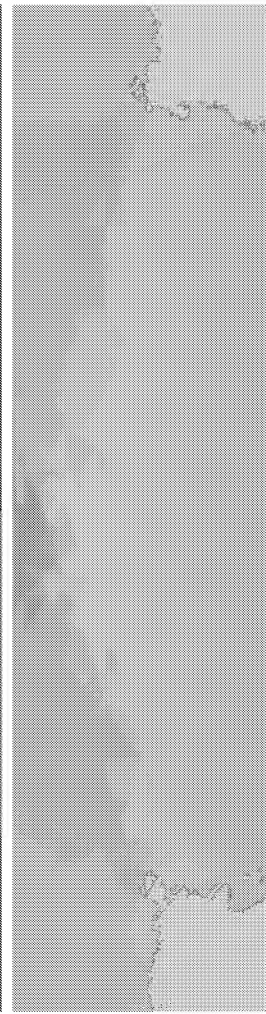
[0052]The multilayer blow molding object (container which is 50 cm by 70 cmx20 cm in height) which performed blow molding respectively and contains a pellet again after mixing polyethylene composition 50 corresponding weight section to 50 % of the weight of each reproduced pellet from which these barrier materials differ was acquired. About the multilayer blow molding object which was acquired about each of four kinds from which a barrier material differs above and which does not contain a recycled material, and the multilayer blow molding object containing the recycled material by repetition path processing, the following test evaluation was carried out and the result was shown in Table 1.

[0053]1) The rate of bending flexibility : JIS K7203 conformity, 23 \*\* (from the drum section flat part of the above-mentioned Plastic solid, the specimen with an 80 mm] in length ] x10-mm thickness of 4\*\*0.5 mm was cut, and measurement was presented) [ in width ]

2) 70 l. of water was injected into the compressive test above-mentioned Plastic solid, and thermal melting arrival of the regio oralis was carried out with the board of the same polyethylene composition as a polyethylene layer. Subsequently, the hole of the diameter of about 8 mm was made in the shoulder of this Plastic solid from the top, the nipple was thrust, and the ball valve was attached to it. This was kept in 53 \*\* oven one whole day and night, 2.94-Pa pressure air was enclosed via the ball valve after that, and the grade of the crack by modification and leak generating was evaluated after 5-hour neglect in 53 \*\* oven.

O : although a crack, \*\*:crack without a leak, and a leak have not resulted, they are x:crack with remarkable modification, and those with a leak. [0054]3) Water / ethylene glycol mixed solution is put into a low-temperature drop impact test profitable \*\*\*\* multilayer blow molding object, Entire weight was 70 kg, the regio oralis was sealed, under -40 \*\*, enough, after cooling, it was made to fall to a concrete face from the height which turns the pinch off part of a multilayer blow molding object down, and is shown in Table 1, the existence of the crack was investigated, and the fall height of the limit was found.

[0055]4) based on the gas barrier examination Ministry of Transport standard, it was filled up with what mixed 20 % of the weight for methanol on the multilayer blow molding object first at about 15 kg of regular gasoline, and this, respectively, and started from the multilayer blow molding object drum section of the same kind -- it was monotonous and enclosed by carrying out thermal melting arrival of the regio



oralis. Based on the Ministry of Transport standard, 20 between was neglected after enclosure to the steaming oven interior of a room adjusted to 40 \*\*, measurement of the weight change with the passage of time was performed, and the average transmission quantity per day was calculated.

[0056]The multilayer blow molding object of the combination shown in Table 2 was fabricated by the same method as an example using polyethylene, high concentration modified polyethylene, barrier layer resin, and glue line resin which were used in the one to comparative example 16 example, and it carried out similarly about reclaimed rubber further. Only about the comparative examples 3 and 4, it fabricated so that the superintendent officer of a multilayer blow molding object might be set to 7 kg. Also about these, it was similarly estimated as the example and the result was shown in Table 2.

[0057]

[Table 1]

	実施例															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
PE-1	85	42.5	75	37.5	75	37.5	75	37.5	75	37.5	65	32.5	75	37.5	75	37.5
PE-3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	10	5
ン	5	2.5	5	2.5	5	2.5	5	2.5	5	2.5	5	2.5	5	2.5	5	2.5
マイカ	10	5	20	10	20	10	20	10	20	10	30	15	-	-	-	-
ガラス繊維	-	-	-	-	-	-	-	-	-	-	-	-	20	10	10	5
ド	-	50	-	50	-	50	-	50	-	50	-	50	-	50	-	50
	BR-1	BR-1	BR-1	BR-1	BR-2	BR-2	BR-3	BR-3	BR-4	BR-4	BR-1	BR-1	BR-1	BR-1	BR-1	BR-1
	AD-1	AD-1	AD-1	AD-1	AD-1	AD-1	AD-1	AD-1	AD-1	AD-1	AD-1	AD-1	AD-1	AD-1	AD-1	AD-1
MPa	1.530	1.490	1.840	1.750	1.820	1.720	1.860	1.690	1.810	1.740	2.510	2.390	1.940	1.630	1.500	1.460
-	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
高さ	>10	>10	>10	8	>10	8	>10	8	>10	8	8	6	>10	6	8	8
g/日/タンク																
	0.2	0.2	0.2	0.2	0.3	0.3	0.8	0.9	0.4	0.4	0.1	0.2	0.2	0.2	0.2	0.2
ノール液	6.8	7.1	6.6	6.9	7.4	7.7	1.3	1.5	0.6	0.8	6.5	6.8	7.5	7.8	6.8	7.2

表1

			ポリエチレン	主層	
			高強度変性 ポリエチレン	重層	
			無炭フィラーマ 力	量	
			再生材ブレンド	%	
			バリア層	構成	
			接着層	形成	
			曲げ弾性率(23℃)	成形	
			耐圧試験	体	
			低温落下衝撃試験	性	
			(限界落下高さ)	能	
			ガスバリアー試験 g/	評	
			ガソリン	価	
			ガソリン/メタノー		
			20重量%混合液		

[0058]

[Table 2]

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
エチレン PE-1	100	50	100	50	100	50	100	50	100	50	50	25	80	40	90	45
PE-3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	10	5
変性 ポリエチレン	-	-	-	-	-	-	-	-	-	-	5	2.5	-	-	-	-
フィラー マイカ	-	-	-	-	-	-	-	-	-	-	45	22.5	20	10	-	-
ガラス繊維	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
材ブレンド	-	50	-	50	-	50	-	50	-	50	-	50	-	50	-	50
	BR-1	BR-1	BR-1	BR-1	BR-2	BR-2	BR-3	BR-3	BR-4	BR-4	BR-1	BR-1	BR-1	BR-1	BR-1	BR-1
	AD-1	AD-1	AD-1	AD-1	AD-1	AD-1	AD-1	AD-1	AD-1	AD-1	AD-1	AD-1	AD-1	AD-1	AD-1	AD-1
率(23℃)	940	950	950	950	940	940	970	970	970	980	3,450	3,270	1,890	1,720	920	930
	△	△	○	○	△	△	△	△	△	△	×	×	○	○	△	△
衝撃試験 高さ	>10	8	>10	>10	>10	8	8	6	8	6	2	2	4	2	8	6
ヤー試験 g/日/タンク (下高さ)																
ン	0.2	0.3	0.2	0.2	0.3	0.3	1.0	1.0	0.5	0.6	0.1	0.2	0.2	0.2	0.2	0.3
ン/メタノール 量%混合液	7.6	7.8	7.4	7.5	8.3	8.4	1.5	1.5	1.0	1.1	6.2	7.5	6.8	7.1	7.7	7.9

表2

	ポリエ		
	主層	高濃度 ポリ	
	(重量%)	無機フ	
	層構成	再生材	
		バリア層	
		接着層	
	成形	曲げ弾性率(	
	体性	耐圧試験	
	能	低温落下耐	
	評価	(限界落下耐	
		ガスバリアヤ	
		ガソリン	
		ガソリン/	
		20重量%	

[0059]

[Effect of the Invention]The multilayer blow molding object of this invention with the gas barrier property which is the characteristic required of an automotive fuel tank etc. Since it is the multilayer hollow body excellent in shock resistance also when it excels in reclaimed rubber nature, such as a barricade, and reclaimed material is included with reclaimed rubber, the industrial-utilizations value is very useful as an automotive fuel tank.

[Translation done.]